JAPANESE / ENGLISH TRANSLATION OF

Japanese Patent Application JP 7 – 149690 A

Title: Method for Manufacturing High-Purity Terephthalic Acid

Your Ref: No. 9143

For: Eastman Chemical Company -
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9109 Eagle Hills Dr . Las Vegas NV 89134 . ph: 866-722-7990 (toll-free) . fax: 702-973-6009
email: sales@tls-translations.com

(19) Japanese Patent Office (JP) **(12) Unexamined Patent Gazette (A)** (11) Unexamined Patent Application No:
Kokai 7-149690
(43) Date of Publication: June 13, 1995

(51) Int. Cl.[6]	Class. Symbols	Internal Office Registration Nos.:	FI	Technical Classification Field
C 07 C 63/26	E	9356-4H		
	J	9356-4H		
	L	9356-4H		
	N	9356-4H		
B 01 J 27/128	X	9342-4G		

Request for Examination: Not yet submitted Number of Claims: 4 OL (Total of 8 pages [in original])

(21) Application No.: 5-299465
(22) Date of Filing: November 30, 1993

(71) Applicant: 000004466
Mitsubishi Gas Chemical Company, Inc.
2-5-2 Marunouchi
Chiyoda-ku, Tokyo
(71) Applicant: 000003160
Toyobo Co., Ltd.
2-2-8 Dojimahama, Kita-ku
Osaka-shi, Osaka-fu
(71) Applicant: 592162324
Mizushima Aroma Co., Ltd.
2-3-1 Mizushima Nakadori
Kurashiki-shi, Okayama-ken
(72) Inventor: Fumio Ogoshi
c/o Mitsubishi Gas Chemical Company, Inc.
3-10 Mizushima Kaigandori
Kurashiki-shi, Okayama-ken
(74) Agent: Tamotsu Otani, Patent Attorney

(54) [Title of the Invention] Method for Manufacturing High-Purity Terephthalic Acid

(57) [Summary]

[Object] To provide a method for manufacturing high-purity terephthalic acid from a terephthalic acid crystal slurry solution derived from the catalytic hydrogenation of crude terephthalic acid obtained by liquid-phase oxidation.

[Constitution of the Invention] The liquid-phase oxidation of *p*-phenylene compounds or the like is carried out in the presence of a cobalt and manganese catalyst and a bromine compound in

an acetic acid solution at a pressure of 10 to 30 atm and a temperature of 150 to 240°C, or in the presence of a cobalt catalyst in an acetic acid solution at a pressure of 5 to 20 atm and a temperature of 100 to 170°C; the resulting crude terephthalic acid is subjected to catalytic hydrogenation in high-temperature water of 200°C or higher in the presence of a Group VIII noble metal catalyst; the catalyst is separated and removed; the temperature and pressure are thereafter reduced to form a terephthalic acid crystal slurry solution; the terephthalic acid crystal slurry solution is brought to a temperature of 120 to 200°C, introduced to a solvent substitution column, and brought into contact with a rising stream of high-temperature water introduced from the lower portion of the solvent substitution column; the mother liquor of the terephthalic acid crystal slurry solution is discharged from the column top and the terephthalic acid crystals are discharged from the column bottom as a slurry together with the high-temperature water; and the terephthalic acid crystals are separated from the slurry discharged from the column bottom.

[Claims]

[Claim 1] A method for manufacturing high-purity terephthalic acid, characterized in that the liquid-phase oxidation of a *p*-phenylene compound (having a carboxyl group and/or a carboxyl group-generating oxidizable substituent group in the para positions) is carried out in the presence of a cobalt and manganese catalyst and a bromine compound in an acetic acid solution at a pressure of 10 to 30 atm and a temperature of 150 to 240°C, or in the presence of a cobalt catalyst in an acetic acid solution at a pressure of 5 to 20 atm and a temperature of 100 to 170°C; the resulting crude terephthalic acid is subjected to catalytic hydrogenation in high-temperature water of 200°C or higher in the presence of a Group VIII noble metal catalyst; the catalyst is separated and removed; the temperature and pressure are thereafter reduced to form a terephthalic acid crystal slurry solution; the terephthalic acid crystal slurry solution is brought to a temperature of 120 to 200°C, introduced to a solvent substitution column, and brought into contact with a rising stream of high-temperature water introduced from the lower portion of the solvent substitution column; the mother liquor of the terephthalic acid crystal slurry solution is discharged from the column top and the terephthalic acid crystals are discharged from the column bottom as a slurry together with the high-temperature water; and the terephthalic acid crystals are separated from the slurry discharged from the column bottom.

[Claim 2] The manufacturing method for high-purity terephthalic acid cited in claim 1, wherein the temperature of the high-temperature water introduced from the lower portion of the solvent substitution column is 5 to 70°C lower than the temperature of the terephthalic acid crystal slurry solution introduced to the solvent substitution column.

[Claim 3] The manufacturing method for high-purity terephthalic acid cited in claims 1 or 2, wherein the terephthalic acid concentration in the terephthalic acid crystal slurry solution extracted from the lower portion of the bottom of the solvent substitution column is made higher than the terephthalic acid concentration of the terephthalic acid slurry crystal solution[1] introduced to the solvent substitution column.

[Claim 4] The manufacturing method for high-purity terephthalic acid cited in claims 1, 2, or 3, wherein crystallization of the terephthalic acid after catalytic hydrogenation is carried out in multiple stages, and the terephthalic acid crystal slurry solution obtained from a mid-stage crystallizer is used for introduction to the solvent substitution column.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a method for manufacturing high-purity terephthalic acid, and more particularly to a method for manufacturing a high purity product with a high degree of whiteness for terephthalic acid, which is a principal crude material for the polyester resins widely used in fibers, film, industrial materials, common molded products, and other products.

[0002]

[Prior Art] Terephthalic acid is ordinarily manufactured using acetic acid as a solvent under high temperature and high pressure by the air oxidation of *p*-xylene in which an accelerator such as a bromine compound or acetic aldehyde has been added to a cobalt or manganese catalyst. However, crude terephthalic acid resulting from this liquid-phase air oxidation normally has inferior whiteness, large quantities of 4-carboxybenzaldehyde (4CBA), *p*-toluic acid, or other impurities are contained therein, and this crude terephthalic acid is not directly suitable for reaction with glycol to form polyester. Methods for manufacturing terephthalic acid have also

[1] Should probably read "terephthalic acid crystal slurry solution"

been proposed whereby acetic is used as a solvent in the same manner as described above, and liquid-phase oxygen oxidation is carried out under high pressure and temperature using a cobalt catalyst, however, the by-production of 4CBA and other impurities is considerable in these methods as well, and, in the same manner as the above-described method, this crude terephthalic acid cannot be directly used in reactions with glycol or the like.

[0003] A large number of methods in which the refining treatment is carried out by oxidation, reduction, or another reaction are known as methods for manufacturing high-purity terephthalic acid from crude terephthalic acid containing 4CBA and other such impurities. For example, a method for hydrogenating an aqueous solution of crude terephthalic acid at a high temperature is disclosed in JP (Kokoku) 41-16860 as a hydrogen reduction refining method, and an improvement method thereof is also disclosed in JP (Kokoku) 47-49049. Proposed in JP (Kokoku) 47-49049 is a process in which the cooling velocity by water evaporation is kept at 2.2 to 5.5°C per minute, and crystal separation is carried out in a temperature range of 120 to 150°C in order to prevent pTOL contamination when crystallizing terephthalic acid from a hydrogenated crude terephthalic acid solution. However, in accordance with an experiment performed by the present inventor, the requirement related to the cooling velocity in the method related to this proposal is such that it is difficult to control the cooling velocity in the continuous crystallization tanks when crystallizing terephthalic acid crystals with a continuous crystallization process whereby the solution passes through crystallization tanks disposed in a straight line. In other words, this method adopts an approach whereby the temperature of the slurry solution is reduced through water evaporation by setting the pressure in each stage of the crystallizer to a pressure that is lower than each previous stage of the crystallizer, but the nature of pressure is such that a completely uniform pressure is created in a single crystallizer. This means that the temperature reduction is essentially performed instantaneously in each crystallizer until a temperature that corresponds to the set pressure is achieved downstream from the metering valve located between the current crystallizer and the previous-stage crystallizer. Therefore, to actually implement the cooling velocity stipulated in JP (Kokoku) 47-49049 with a continuous crystallization method, a crystallization tank with twenty stages or more is required, and is not practical from the aspect of industrial production.

[0004] The above-described cooling velocity is preferably implemented in a batch-type crystallization method because the cooling velocity itself can be relatively freely controlled, but

the present inventor and others, as a result of actual experimentation with the batch-type crystallization method, could not find any particular technical objection to the cooling velocity of 2.2 to 5.5°C itself. The specification of a crystal separation temperature (which is another issue) can be said to be effective in inhibiting pTOL contamination in the terephthalic acid crystals.

[0005] The invention cited in JP (Kokoku) 47-49049 as a method for separating crystals from a crystal slurry proposes the use of centrifugal separation, filtering, and other methods, but the method that can be practically implemented on a commercial scale is currently limited to centrifugal separation. Centrifugal separation entails introducing a slurry solution to a basket rotating at a high speed, causing the mother liquor to overflow from the top portion, and inducing crystallization to occur in the lower portion. However, there are a number of drawbacks in the structure and function of centrifugal separation, and one of those drawbacks is that it is difficult to wash the crystals. In other words, the amount of mother liquor adhering to the crystals increases, and a method for reslurrying the separated terephthalic acid cake with high-temperature water is ordinarily adopted to solve this problem, but this creates a new problem in that the separation step must be repeated. This is less preferable in that daily maintenance and management of the apparatus is laborious because of the need to carry out centrifugal separation at a high temperature and pressure with a high-speed rotation, the apparatus is different that an ordinary centrifugal separator, and higher capital investment is needed. An improvement method for performing filtration at high temperature and high pressure has been proposed to overcome the drawbacks of centrifugal separation. The use of a rotary vacuum filter at high temperature and pressure was suggested in JP (Kokai) 1-299618, for example, but the technique itself is not particularly novel, and is not a realistic concept that can be implemented on a commercial scale. Also proposed are several methods that apply a liquid cyclone separator, but all of these have an inadequate substitution ratio for the mother liquor.

[0006] As a result of thoroughgoing research concerning a solution to these drawbacks, the present inventor conceived the idea of substituting the mother liquor of the terephthalic acid slurry solution with fresh water using a solvent substitution column. Furthermore, it was empirically confirmed that a considerable effect that is not limited to a simple mother liquor substitution effect could be demonstrated by specifying the conditions of the solvent substitution column. In particular, it was found that the crystallization and separation of high-purity terephthalic acid after catalytic hydrogenation in the high-temperature water, and the separation

and removal of the catalyst are such that the pTOL concentration is lower the greater the internal crystallization of the terephthalic acid is, the pTOL concentration is conversely higher the nearer to the surface the crystals are, and the pTOL concentration is higher the smaller crystal grains are. It was furthermore found that crystallizing terephthalic acid in a high-temperature range alone, and washing the formed crystals in a high-temperature range is very effective in achieving the object of the present invention.

[0007]

[Problems to Be Solved by the Invention] Therefore, based on these discoveries, an object of the present invention is the perfection of a manufacturing method for high-purity terephthalic acid, having discovered an effective method of treating a terephthalic acid crystal slurry solution after catalytic hydrogenation of liquid containing crude terephthalic acid resulting from liquid-phase oxidation.

[0008]

[Means Used to Solve the Above-Mentioned Problems] The present inventor, as a result of research concerning a solution to the above-stated problems, discovered that substituting the terephthalic acid crystal slurry solution using a prescribed method after catalytic hydrogenation is most effective, and the present invention was perfected based on this discovery. In other words, the main point of the present invention is a method for manufacturing high-purity terephthalic acid characterized in that the liquid-phase oxidation of a *p*-phenylene compound (having a carboxyl group and/or a carboxyl group-generating oxidizable substituent group in the para positions) is carried out in the presence of a cobalt and manganese catalyst and a bromine compound in an acetic acid solution at a pressure of 10 to 30 atm and a temperature of 150 to 240°C, or in the presence of a cobalt catalyst in an acetic acid solution at a pressure of 5 to 20 atm and a temperature of 100 to 170°C; the resulting crude terephthalic acid is subjected to catalytic hydrogenation in high-temperature water of 200°C or higher in the presence of a Group VIII noble metal catalyst; the catalyst is separated and removed; the temperature and pressure are thereafter reduced to form a terephthalic acid crystal slurry solution; the terephthalic acid crystal slurry solution is brought to a temperature of 120 to 200°C, introduced to a solvent substitution column, and brought into contact with a rising stream of high-temperature water

introduced from the lower portion of the solvent substitution column; the mother liquor of the terephthalic acid crystal slurry solution is discharged from the column top and the terephthalic acid crystals are discharged from the column bottom as a slurry together with the high-temperature water; and the terephthalic acid crystals are separated from the slurry discharged from the column bottom.

[0009] The specific details of the present invention are described below. Crude terephthalic acid can be obtained by liquid-phase oxidation of *p*-phenylene compounds, but the *p*-phenylene compounds to be used are ones having a carboxyl group and/or an oxidizable substituent group that generates a carboxyl group through liquid-phase oxidation that is present at the respective para positions. Examples of the substituent group include the methyl group, ethyl group, propyl group, isopropyl group, aldehyde group, and acetyl group. These substituent groups may be mutually the same or different.

[0010] Oxygen or air may be used as the oxidizing agent in the oxidation in the liquid phase, and there is no particular limitation to either of these, but air is adequate for oxidation in the presence of the cobalt or manganese catalyst and a bromine compound cocatalyst in an acetic acid solution. When oxidizing in the presence of a cobalt catalyst in an acetic acid solution, oxygen itself is preferred.

[0011] As a catalyst, a bromine compound can be jointly used when a cobalt or manganese catalyst is employed. The bromine compound is normally regarded as cocatalyst, and hydrogen bromide or sodium bromide is preferred in particular. When a cobalt catalyst is used, acetaldehyde, methyl ethyl ketone, or the like is preferably jointly used as an accelerator.

[0012] The crude terephthalic acid resulting from liquid-phase oxidation in an acetic acid solution ordinarily contains a considerable amount of impurities such as 4CBA, and the OD340 value (which is an index of whiteness) is also not at a level that allows the product to be directly used as a polymer crude material for molding, so an impurity treatment or another aftertreatment step is required. The quantity of 4CBA or other impurities in the crude terephthalic acid is not, however, particularly limited in the post-treatment step. The same also applies to OD340. The combustion loss of acetic acid due to the oxidation reaction can be inhibited by selecting oxidation reaction conditions whereby the 4CBA content is increased to a certain extent, so it is advantageous for the entire process that the 4CBA content in the crude terephthalic acid be set to 500 ppm or greater in the liquid-phase oxidation step.

[0013] The crude terephthalic acid solution is subsequently moved to the catalytic hydrogenation step. The catalytic hydrogenation is carried out a high temperature and pressure so that the process is performed in a solution state. The catalytic hydrogenation is performed at a temperature 200°C or higher, and preferably 240 to 300°C, in the presence of hydrogen. The concentration of the crude terephthalic acid is preferably in a range of 10 to 40 wt%, so it is preferable to establish a pressure that is adequate for maintaining a liquid phase and ensuring a partial hydrogen pressure suitable for a catalytic hydrogenation reaction, normally in a range of 30 to 80 atm.

[0014] A Group VIII noble metal is used as the catalyst for the catalytic hydrogenation reaction. The Group VIII noble metal is preferably palladium, platinum, ruthenium, or rhodium, but particularly preferred is palladium or platinum. These metals are not necessarily used alone, and two or more may be compounded and used as required.

[0015] The above-described catalyst is not necessarily limited to being used while supported on a carrier, but it is ordinarily convenient to do so. A porous substance is normally used as the carrier, but materially preferred is a carbon-based carrier, and activated carbon and particularly cocoanut charcoal is advantageous. Even a small amount of catalyst supported by the carrier is effective, and the range is not particularly limited, but a supported amount of about 0.1 to 0.5 wt% is advantageous for maintaining long-term activity.

[0016] The amount of hydrogen that must be supplied for catalytic hydrogenation is at least two or more molar amounts with respect to 4CBA. The catalytic hydrogenation should last for a time that is sufficient to essentially allow the hydrogenation reaction to progress, and is ordinarily in a range of 1 to 60 minutes, and preferably 2 to 20 minutes. Catalytic hydrogenation is normally performed with the continuous method.

[0017] The crude terephthalic acid solution subjected to catalytic hydrogenation prevents contamination from fine powder caused, for example, by abrasion of the activated carbon used as the catalytic carrier, so terephthalic acid crystals are formed and a slurry solution is produced by filtering the solution with a filter manufactured using sintered titanium or another sintered metal or carbon particles, thereafter introducing the solution to a batch-type crystallizer or a crystallizer with two to six stages linked in series, and sequentially reducing the pressure in the crystallizer to lower the temperature to 120 to 200°C by moisture evaporation. Preferably used in this case is a slurry solution, obtained from an intermediate-stage crystallizer in the multistage

crystallization of catalytically hydrogenated terephthalic acid, as the terephthalic acid crystal slurry solution introduced to the solvent substitution column.

[0018] The terephthalic acid crystal slurry composed of the mother liquor and terephthalic acid crystals obtained in this manner is added in the solvent substitution step, that is to say, the separation step in which the mother liquor containing a considerable quantity of impurities is substituted with fresh water. A specific example of the operating method of the solvent substitution column is described below. The terephthalic acid slurry solution is conveyed through the upper portion of the column into the rising stream of high-temperature water that has been introduced from the column bottom. The temperature of the high-temperature water is set essentially to the same level as the terephthalic acid slurry solution, but the solvent substitution efficiency can be increased by setting the temperature thereof several degrees higher, as described below. The pressure should be sufficient to maintain the temperature of the high-temperature water, and substantially automatically determined once the temperature is set. The linear velocity of the rising liquid stream of high-temperature water varies in accordance with the structure of the device, the crystal size, and other factors, but is preferably about 0.001 to 0.01 m/sec. If the linear velocity is excessively low, the separation of the terephthalic acid crystals from the mother liquor is inadequate, and the purity of the terephthalic acid is reduced. If the linear velocity is conversely excessively high, there is a drawback in that more high-temperature water is used.

[0019] The structure of the solvent substitution column must be such that the rising liquid stream of high-temperature water rises with a certain linear velocity without back-mixing, so a columnar shape is preferred. In order to achieve this aim, a column having suitable baffles, a porous plate column, or the like is advantageous. An agitator is not necessarily required in the column, but providing an agitator is effective for the purpose of improving contact between the high-temperature water and the crystals and removing from the crystals the mother liquor that accompanies crystallization in the process for suspending and precipitating the crystals in the high-temperature water. The use of a so-called RDC (Rotary Disk Contactor) is particularly recommended for achieving this aim.

[0020] The results of experimentation were entirely unexpected in the sense that the solvent substitution efficiency was increased by setting the temperature of the high-temperature water introduced from the column bottom to a value lower than the temperature of the terephthalic acid

slurry removed from the upper portion of the column as described above. A theoretical description of this phenomenon is very difficult at this point. This is due to the large number of factors required for a theoretical explanation, and to the fact that there are interacting phenomena among these factors. However, considering the current experimental information obtained by the present inventor, it is possible to consider this to be the result of minimizing back-mixing in the rising liquid stream of high-temperature water by setting the temperature in the column bottom to a value that is lower than the temperature of the column top.

[0021] As described above, this phenomenon provides extremely advantageous conditions and recommended parameters for manufacturing high-purity terephthalic acid, and establishing the condition whereby the temperature of the high-temperature water is set to a low value creates an effect whereby the required cost of heating for solvent substitution can be reduced and a terephthalic acid with higher purity can be manufactured. A detailed study of the temperature conditions indicates that a further advantage can be provided in that there is the possibility of improved quality through an increase the purity of the terephthalic acid.

[0022] However, setting the temperature of the high-temperature water low and maintaining a large temperature difference between the high-temperature water and terephthalic acid slurry is limited as such, and various problems tend to arise in overcoming this limitation. For example, the precipitation velocity of the crystals decreases, and the column diameter of the substitution column must be increased in order to maintain the same rate of manufacture. This not only leads to an increase in capital spending, but also makes it difficult to control the rising liquid stream of high-temperature water in an orderly manner, and compromises the effect of improved quality. Considering these factors overall, the temperature of the high-temperature water to be introduced to the solvent substitution column should be in a range of about 5 to 70°C lower than the temperature of the terephthalic acid that is to be introduced.

[0023] By adopting the solvent substitution step of the present invention, the terephthalic acid concentration in the slurry solution after solvent substitution can be increased if adjustments are made to the input and discharge rates of the materials to and from the solvent substitution column. As a result of this effect, it has not only become possible to cut back on the amount of fresh hot water introduced to the solvent substitution column, but the load in the following crystal separation operation can also be reduced for the slurry discharged from the column bottom. Describing this effect in greater detail, if the sole object is simply to decrease the

amount of hot water and reduce the load in the separation operation, this can be achieved by increasing the concentration of the terephthalic acid slurry solution to be introduced to the column. However, experimental results obtained by the inventor and others support the fact that if the slurry concentration fed to the solvent substitution column is increased, the concentration of the impurities in the mother liquor in the crystallization step increases by an amount equivalent thereto. As a result, the components that raise the OD340 value described above are taken in by the terephthalic acid crystals, and the concentration of impurities increases. In other words, the present invention now makes it possible to ensure that the slurry concentration in the substitution column is increased in order to simultaneously satisfy two opposing requirements, namely, that the crystal terephthalic purity in the slurry solution fed to the solvent substitution column be made as high as possible, and that the load in the crystal separation operation and the amount of hot water be reduced.

[0024] The mother liquor discharged from the column top contains, in slurry form, terephthalic acid that corresponds to the solubility at the temperature of the liquor, and fine terephthalic acid crystals discharged in conjunction with the rising stream. This liquid flow passes through one to three crystallization tanks disposed in series, so the liquid flow is cooled to the minimal possible temperature to form terephthalic acid crystals. The terephthalic acid is separated and recovered from the mother liquor with a filter or another suitable device, and returned to the acid reaction system to be efficiently reused. Terephthalic acid that corresponds to the solubility at that temperature and other organic components are contained in the mother liquor discharged from the crystal collector, so the mother liquor may be passed through a further recovery step or sent directly to a waste treatment step.

[0025] The liquid flow discharged from the lower portion of the solvent substitution column is a slurry solution of high-temperature water that contains refined terephthalic acid crystals. The liquid flow is passed through one to three crystallization tanks disposed in series, and is cooled to 70 to 110°C. The terephthalic acid is formed into crystals; and the crystals are thereafter separated in the crystal separator, discharged, and dried in a drier, yielding high-purity terephthalic acid. The mother liquor discharged from the crystal separator contains only terephthalic acid corresponding to the solubility at that temperature, and other organic and inorganic impurities are at a very low concentration. The mother liquor is reused in the catalytic hydrogenation step. The terephthalic acid crystal slurry solution at a temperature of 120 to

200°C is introduced to the solvent substitution column at that temperature, and is brought into contact over the widest possible surface area with the rising stream of fresh high-temperature water introduced from the lower portion of the solvent substitution column. The mother liquor in the slurry is discharged from the column top, terephthalic acid crystals are discharged from the column bottom as a slurry solution together with the high-temperature water, and the high-purity terephthalic acid crystals are separated from the slurry solution discharged from the column bottom.

[0026] In this case, the temperature of the high-temperature water introduced to the lower portion of the solvent substitution column is preferably lower than the temperature of the terephthalic acid slurry solution introduced to the upper portion of the column, and is more preferably adjusted so as to be about 5 to 70°C lower, to increase the solvent substitution effect, as described above. The amount of slurry and hot water to be introduced is preferably adjusted so that the terephthalic acid concentration in the terephthalic acid slurry solution discharged from the bottom of the column is greater than the terephthalic acid concentration in the terephthalic acid slurry solution fed to the upper portion of the column.

[0027] The mechanism whereby high-purity terephthalic acid is obtained from crude terephthalic acid produced by liquid-phase oxidation and hydrogenation in accordance with the solvent substation operation of the present invention is not yet understood. It should be noted that this effect, as also mentioned in JP (Kokoku) 47-49049, cannot be explained by the solubility of pTOL in terephthalic acid. The extensive experience and experimentation of the present inventor and others over many years suggest that this is a phenomenon that is commonly attributed to eutectic crystals, and a rational explanation can be offered in that it is assumed that pTOL is taken into the crystals with a certain distribution coefficient in the terephthalic acid crystallization process and that this distribution coefficient varies at an exponential rate in relation to the temperature. In other words, it is reasonable to assume that the distribution coefficient is low at high temperatures and becomes higher at an accelerated rate with lower temperatures.

[0028] These effects are not limited solely to effects related to the separation of pTOL. The same effects are also observed in other impurities (although to a lesser extent) in the reduction of 4CBA and a lower OD340 value, for example. In other words, in accordance with the experimental results of the present inventor and others, pTOL has the greatest temperature

correlation of the distribution coefficients, and the correlation is lower for 4CBA and OD340. That is to say, the effect when crystal separation is performed at high temperature is greater for pTOL, and smaller for 4CBA and OD340.

[0029] The present invention is described below with working examples.

[Working Examples]

(Working Example 1) Crude terephthalic acid was manufactured using a commercial-scale apparatus, manganese acetate or cobalt acetate as the catalyst, and hydrogen bromide as the cocatalyst; and *p*-xylene was oxidized with air in a hydrated acetic acid solvent at a temperature of 205°C and pressure of 17 atm. Next, 200 mL of a catalyst in which 0.5% palladium was supported on activated carbon was loaded into a stainless steel pressure reaction column that was equipped with an external heating device and had a length of 350 mm and an inside diameter of 26 mm, the reaction column was heated to 285°C, and a 30% aqueous solution of crude terephthalic acid heated to 285°C was fed from the column top at a rate of 1,400 g per hour. Hydrogen gas was fed from a hydrogen gas supply line to the terephthalic acid aqueous solution at a rate of 0.4 NL per hour to carry out catalytic hydrogenation. The reaction liquid that flowed from the bottom of the reaction column was passed through a buffer tank provided for adjusting the difference between the supply and discharge velocities, cooled to normal temperature, and discharged as a slurry solution to a receptacle outside the reaction column by means of an intermittent discharge device composed of a three-way valve and an actuator. The solvent substitution column that was used was composed of stainless steel and was equipped with an external jacket with an inside diameter of 25 mm and a height of 1,500 mm, the slurry solution introduction port was disposed in a position 1,300 mm from the bottom surface, and the hot water introduction port was disposed in a position 100 mm from the bottom surface. Receptacles with a capacity of 50 L were connected to the respective discharge ports at the top and bottom of the column, and a heating device, reflux condenser, agitating device, and liquid surface detection device were mounted on the receptacle. In advance of operation, hot oil at a temperature of 150°C is circulated to the external jacket, high-temperature water heated to 150°C was introduced through the high-temperature water introduction port at a rate of 1,880 g per hour, and the hot water was discharged from the discharge ports at the top and bottom of the column to a receptacle when the column became filled with hot water. Next, the slurry solution heated to

150°C and passed through the above-described catalytic hydrogenation step was introduced from the slurry solution introduction port at a rate of 2,470 g per hour, and the slurry solution was discharged from the bottom of the column at a rate of 1,790 g per hour. The slurry solution containing fine crystals was discharged from the column top at a rate of 2,560 g per hour. The temperature of the receptacle at the bottom of the column was reduced to 90°C. The slurry solution was held for about 15 minutes, thereafter discharged, and rapidly filtered with an adequately heated G3 glass filter. The crystals were then washed with hot water and dried. As a result, the slurry solution with a terephthalic acid concentration of 30 wt% introduced to the column was discharged from the bottom of the column as a slurry in which the terephthalic acid concentration was 40 wt%. Terephthalic acid (total amount in a solution state and as fine crystals) was discharged from the column top at a rate of 24 g per hour. This corresponds to 3 wt% of the terephthalic acid introduced to the column in terms of terephthalic acid. The analyzed values of the resulting terephthalic acid crystals are as noted in Table 1.

[0030] (Working Example 2) The temperature of the solvent substitution step was set to 200°C, and in this example the hot water introduction rate was set to 2,290 g per hour, the slurry solution introduction rate to 3,710 g per hour, and the slurry solution discharge rate from the bottom of the column to 2,570 g per hour. This is a required modification to keep the crystal precipitation rate in the upper portion of the column at the same level as that in Working Example 1. Other conditions were kept the same as described in Working Example 1. As a result, the slurry solution with a terephthalic acid concentration of 30% introduced to the column was discharged from the bottom of the column as a slurry in which the terephthalic acid concentration was 40%. Terephthalic acid (total amount in a solution state and as fine crystals) was discharged from the column top at a rate of 87 g per hour. This corresponds to 8% of the terephthalic acid introduced to the column. The analyzed values of the crystals are as noted in Table 1.

[0031] (Working Example 3) The temperature of the solvent substitution step was set to 120°C, the hot water introduction rate to 1,540 g per hour, the slurry solution introduction rate to 1,620 g per hour, and the slurry solution discharge rate from the bottom of the column to 1,180 g per hour. This is a required modification to keep the crystal precipitation rate in the upper portion of the column at the same level as that in Working Example 1. Other conditions were kept the same as described in Working Example 1. As a result, the slurry solution with a terephthalic acid concentration of 30% introduced to the column was discharged from the bottom of the

column as a slurry in which the terephthalic acid concentration was 40%. Terephthalic acid (total amount in a solution state and as fine crystals) was discharged from the column top at a rate of 13 g per hour. This corresponds to 3% of the terephthalic acid introduced to the column. The analyzed values of the crystals are as noted in Table 1.

[0032] (Working Example 4) The external jacket mounted on the solvent substitution column was partitioned into upper and lower portions in a position 700 mm from the bottom surface, hot oil at a temperature of 150°C was circulated to the upper portion of the jacket, and hot oil at a temperature of 140°C was circulated to the lower portion of the jacket. Hot water heated to 140°C was introduced through the hot water introduction port, and a slurry solution heated to 150°C and passed through the above-described catalytic hydrogenation step was introduced from the slurry solution introduction port. Other conditions were kept the same as described in Working Example 1. The analyzed values of the crystals are as noted in Table 1.

[0033] (Comparative Example 1) The temperature of the solvent substitution step was set to 90°C, the hot water introduction rate to 1,220 g per hour, the slurry solution introduction rate to 830 g per hour, and the slurry solution discharge rate from the bottom of the column to 610 g per hour. This is a required modification to keep the crystal precipitation rate in the upper portion of the column at the same level as that in Working Example 1. Other conditions were kept the same as described in Working Example 1. As a result, the slurry solution with a terephthalic acid concentration of 30 wt% introduced to the column was discharged from the bottom of the column as a slurry in which the terephthalic acid concentration was 40 wt%. The analyzed values of the crystals are as noted in Table 1.

[0034] (Comparative Example 2) The slurry solution that had passed through the catalytic hydrogenation step in working example 1 was held for 15 minutes at 90°C and rapidly filtered with an adequately heated G3 glass filter. The crystals were thereafter washed with hot water and dried. The analyzed values of the crystals are as noted in Table 1.

[0035]

[Table 1]

	Temperature of solvent substitution column (°C)	Terephthalic acid extracted from the column top (wt%)	Analytical value of the refined terephthalic acid		
			pTOL (ppm)	OD340	4CBA (ppm)
Crude TA	-	-	92	1.5	2930
Working example 1	150	3	104	0.080	6
Working example 2	200	8	26	0.036	2
Working example 3	120	3	148	0.086	7
Working example 4	150 (High-temperature water: 140°C)		83	0.079	6
Comparative example 1	90	2	237	0.091	9
Comparative example 2	-	-	268	0.101	9

TA: Terephthalic acid
pTOL: *p*-toluic acid
4CBA: 4-carboxybenzaldehyde

[0036] The column titled "Terephthalic acid extracted from the column top (wt%)" in the table contains values expressed as percent by weight when the entire amount of terephthalic acid (TA) introduced to the column is taken to be 100. The following is apparent from the working and comparative examples in Table 1.

(1) When the solvent is substituted at 150°C, the *p*-toluic acid concentration in the refined terephthalic acid is sharply reduced in comparison with comparative example 2, in which solvent substitution was not performed.

(2) The *p*-toluic acid concentration in the terephthalic acid decreased as the solvent substitution was performed at a higher temperature, but the amount of terephthalic acid drawn from the column top increased and the crystal recovery load in the downstream also increased.

(3) The *p*-toluic acid concentration in the terephthalic acid increased as the solvent substitution was performed. In comparative example 1, in which solvent substitution was carried out at 90°C, the quality merely increased slightly in comparison with comparative example 2, in which solvent substitution was not performed.

(4) The above descriptions are the conclusions regarding the *p*-toluic acid in the terephthalic acid, but it is also apparent from the table that while its effect as an impurity is small, that OD340 values exhibit the same behavior.

(5) The effect on 4CBA is even less than the OD340 values, but it is also apparent that the same behavior is exhibited.

(6) In working example 4, in which the temperature of the introduced slurry solution was 150°C and the temperature of the introduced high-temperature water was 140°C, the concentration of *p*-toluic acid in the refined terephthalic acid was further reduced in comparison with working example 1, in which both temperatures were 150°C. However, the OD340 value and the 4CBA concentration did not change.

[0037]

[Effect of the Invention] It was found that the purity of terephthalic acid crystals can be considerably improved and high quality, high-purity terephthalic acid can be continuously manufactured with a simple method whereby a crude terephthalic acid aqueous solution is subjected to catalytic hydrogenation and the slurry solution is thereafter brought into contact with a rising liquid stream of high-temperature water.

[Amendments]

[Filing Date] February 10, 1994

[Amendment 1]

[Amended Document Name] Specification

[Amended Section] 0018

[Method of Amendment] Modification

[Content of the Amendment]

[0018] The terephthalic acid crystal slurry composed of the mother liquor and terephthalic acid crystals obtained in this manner is added in the solvent substitution step, that is to say, the separation step in which the mother liquor containing a considerable quantity of impurities is substituted with fresh water. A specific example of the operating method of the solvent substitution column is described below. The terephthalic acid slurry solution is conveyed

through the upper portion of the column into the rising stream of high-temperature water that has been introduced from the column bottom. The temperature of the high-temperature water is set essentially to the same level as the terephthalic acid slurry solution, but the solvent substitution efficiency can be increased by setting the temperature thereof several degrees higher, as described below. The pressure should be sufficient to maintain the temperature of the high-temperature water, and is substantially automatically determined once the temperature is set. The linear velocity of the rising liquid stream of high-temperature water varies in accordance with the structure of the device, the crystal size, and other factors, but is preferably about 0.0001 to 0.001 m/sec. If the linear velocity is excessively low, the separation of the terephthalic acid crystals from the mother liquor is inadequate, and the purity of the terephthalic acid is reduced. If the linear velocity is conversely excessively high, there is a drawback in that more high-temperature water is used.

(Continued from front page)

(51) Int. Cl.[6]		Class. Symbols	Internal Office Registration Nos.:	FI	Technical Classification Field
B 01 J	31/04				
C 07 C	51/265				
// C 07 B	61/00	300			